HYLEBOS CLEANUP COMMITTEE RESPONSES TO EPA COMMENTS:

TECHNICAL REVIEW OF REVISED (21 December 1995) DRAFT EVENT 1A AND 1B DATA REPORT - HYLEBOS WATERWAY PRE-REMEDIAL DESIGN PROGRAM

GENERAL RESPONSE

This document responds to EPA's Comments dated February 28, 1996 on the Hylebos Cleanup Committee's (HCC's) Draft Event 1A and 1B Data Report dated December 21, 1995. In its Comments, EPA requires the HCC to make several revisions to the Data Report with which the HCC does not agree. The HCC believes that some of the revisions required by EPA are not supported by the data, are not appropriate under CERCLA, and are arbitrary and capricious. The HCC continues to believe that the analysis contained in the December 21, 1995 Data Report is appropriate. This response is filed for inclusion in the Administrative Record to preserve the HCC's objections to EPA's revisions. Presently, EPA and the HCC are working to establish a process that may result in mutually acceptable resolutions of the issues raised by EPA's required revisions. The HCC reserves all of its rights, including its rights to dispute resolution under the AOC, should the AOC not be amended or the issues not be amicably resolved in the future.

SPECIFIC RESPONSES

Subject to the above objections, and for the Administrative Record, the HCC responds to EPA's comments as follows. Written EPA comments on the revised draft Data Report are reiterated below, followed by the HCC response in italic print. The specific EPA comment or request being responded to is underlined.

A technical review of the revised (21 December 1995) draft Event 1A and 1B Data Report was performed by EPA, its contractor, R. F. Weston, COE, the State, and natural resource agencies. The purpose of the review was to ensure that the data report was revised by the Hylebos Cleanup Committee's (HCC's) contractor in accordance with previous comments received on prior versions, in addition to items discussed during a series of meetings and conference calls. Major additions and/or revisions to the document requiring technical review included:

- Incorporation and interpretation of the natural resource trustees (Trustees) chemical and biological data (including chemical data quality and the selection and use of in-waterway stations as benthic reference locations) in the evaluation of preliminary sediment management areas.

- Inclusion and interpretation of the echinoderm bioassay test results (as re-run by the HCC's contractor) in the evaluation of preliminary sediment management areas.

- Incorporation and use of sediment profile image (SPI) survey data to characterize physical seafloor characteristics and benthic habitats.

- Proposal of an AET for tributyltin (TBT).
- Interpretation of organic enrichment (particularly woodwaste) within the context of a Superfund cleanup.
- Evaluation of risks to human health from ingestion of PCB-contaminated fish and shellfish using modified assumptions.
- Approach to natural recovery evaluations.

General comments related to the above items that may require additional discussions with or clarifications from the HCC are presented first, followed by specific comments related to specific technical issues or editorial comments.

GENERAL COMMENTS

Trustee Chemical Data Quality

Comment G1a: Reviewers have evaluated the arguments presented by the HCC regarding the quality of the Trustee data for extractable organic compounds. Trustee QA/QC methods were somewhat modified from EPA protocols. However, EPA and Weston's review of the information provided in the Trustee QC reports indicates that, with a few minor exceptions, the Trustee data fall within EPA guidelines and are acceptable for use. In addition, EPA concurs with NOAA's conclusions about data quality in their February 7, 1996 letter (attached). Additional details are provided below.

> **G1a Response:** *The HCC continues to believe that the Trustee organics data are biased high based on two sets of observations:*
>
> *First, the Trustee's results of multiple analyses of a certified reference material (NIST 1941) exceeded the certified mean plus the 95 % confidence limit by up to 43.8 percent [certified concentrations are established independently by the National Institute of Standards and Technology (NIST)]. Examples of high bias relative to NIST certified results are provided in the response to Comment G1b.*
>
> *Second, the HCC's chemical results that were generated in the same area of the waterway were consistently less than the Trustee's concentrations. The distribution of hexachlorobutadiene in Hylebos Waterway provides an example of the high bias relative to the HCC's data. Exceedances of the hexachlorobutadiene SQO in the HCC data set are only found in Segment 5 from approximately the AK-WA/Occidental Chemical Corporation property line to the 11th Street bridge. In comparison, exceedances of the SQO in the Trustee data set extend out of the mouth of the waterway through Segments 5, 4, and 3, to Station HY-21 which is over half way up Segment 2.*

Standard Reference Material Results

Comment G1b: Standard reference material SRM 1941, obtained from the National Institute of Standards and Technology (NIST) was analyzed for polycyclic aromatic hydrocarbons with each of six laboratory analytical batches. All results were within the 95% confidence interval for the certified concentrations except for the following:

Sample Number	Analyte	95% Conf. Int. (µg/kg)	Trustee Result (µg/kg)	Trustee Result Percent above 95% UCL
110-111	phenanthrene	337 - 859	910	5.9 %
	fluoranthene	637 - 1971	2000	1.5 %
110-130	phenanthrene	337 - 859	900	4.8 %
	fluoranthene	637 - 1971	2100	6.5 %
	pyrene	572 - 1728	1800	4.2 %

Discussions concerning analyte concentrations above mean certified SRM concentrations are not appropriate. Since SRM 1941 is a homogenized, environmental sample, it is not possible to determine the true or absolute concentration of analytes and "accepted" or "certified" values are only the average of a number of determinations using several analytical methods. It is only possible to determine the probable concentration range for the mean at a specified confidence level, typically 95%.

Based on the PAH analytical results for SRM 1941, trustee data meet accuracy criteria.

G1b Response: *It appears that there is a lack of understanding within EPA regarding the appropriate uses of standard reference materials (SRMs).*

First, SRMs are the most appropriate tool available to determine data accuracy and comparability. Regardless of the number of calibrations conducted or matrix spike or surrogate recoveries measured, the most appropriate measure of accuracy is to compare results to independently derived or known concentrations.

Comment G1b states "Discussions concerning analyte concentrations above mean certified SRM concentrations are not appropriate." In fact, such discussions are highly appropriate. While it is correct that SRM 1941 is a homogenized environmental sample, the 95 percent confidence interval appropriately accounts for environmental variability associated with both the heterogeneous nature of the sample as well as using a variety of analytical methods to analyze the sample. That is the reason that data are compared to the 95% confidence interval and not a single value.

The Combined Quality Assurance Project Plan and Laboratory Analysis Plan for the Commencement Bay Damage Assessment Studies (EVS 1994) states the following objectives for various quality control samples:

- *Initial Calibration (Section 7.1.4.1) - "Instrument blanks or continuing calibration blanks provide information on the stability of the baseline established."*

- *Standard Reference Materials (Section 7.1.4.2) - "Analysis of reference materials and certified reference materials provides information on the* ***accuracy*** *(bolding added) of the laboratory performing the analysis."*

- *Matrix Replicates (Section 7.1.4.3) - "Analytical replicates provide information on the precision of the analysis procedures and are useful in assessing potential sample heterogeneity and matrix effects."*

- *Matrix Spikes and Matrix Spike Duplicates (Section 7.1.4.4) - "Analysis of matrix spike samples provides information on the extraction efficiency of the method on the sample matrix. by performing duplicate matrix spike analyses, information on the precision of the method is also provided for organic analyses."*

- *Surrogate Spikes (Section 7.1.4.5) - "All project samples to be analyzed for organic compounds will be spiked with appropriate surrogate compounds as defined in the analytical methods."*

- *Method Blanks (Section 7.1.4.6) - Method blanks are analyzed to assess possible laboratory contamination of samples associated with all stages of preparation and analysis of sample extracts."*

Thus the project QAPP for the NRDA program calls for using SRMs to assess accuracy! None of the other quality control samples is run to assess accuracy. Why did the National Marine Fisheries Service run SRM samples if not to assess accuracy?

Second, as shown on the following page, which is Table 2D-p1 from the NMFS data, the NMFS laboratory has created larger confidence limits within which to assess their own data. The certified concentrations shown on the following page for SRM 1941 include a mean and a 95% confidence interval. The 95% confidence interval is also shown on the NIST Certificate of Analysis for SRM 1941 which follows Table 2D-p1 in this Comment Response document. Also shown on Table 2D-p1 are upper and lower confidence limits (UCL and LCL, respectively). The UCL and LCL are defined as the mean plus or minus the 95% confidence interval plus or minus an <u>additional</u> 35%, respectively. The UCL and LCL are the limits against which NMFS has assessed their data, not the independently established and certified mean plus or minus the 95% confidence interval.

Table 9D-pt1. QA: Concentrations (ng/g, dry weight) of aromatic hydrocarbons in method blanks and standard reference material (SRM 1941) analyzed as part of the Hylebos Damage Assessment Project.

Sample #	Sample Type	NPH	2MN	ACY	ACE	FLU	PHN	ANT	FLA	PYR	BAA	CHR	BFLA	BAP	IDP	DBA	BZP
Method blank																	
110-073	Method blank	< 0.5	< 0.7	< 0.5	< 0.8	< 0.6	< 0.4	< 0.4	< 0.4	< 0.4	< 0.5	< 0.4	< 0.4	< 0.5	< 0.6	< 0.6	< 0.5
110-092	Method blank	< 0.4	< 0.7	< 0.4	< 0.7	< 0.6	< 0.4	< 0.4	< 0.4	< 0.3	< 0.4	< 0.4	< 0.4	< 0.4	< 0.5	< 0.5	< 0.5
110-112	Method blank	< 0.8	< 1	< 0.9	< 1	< 1	< 0.8	< 0.8	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.8	< 1	< 1	< 0.9
110-131	Method blank	1	< 1	< 0.9	< 1	< 1	< 0.8	< 0.8	2	1	< 0.6	< 0.6	< 0.6	< 0.7	< 0.9	< 0.8	< 0.8
110-156	Method Blank	< 2	< 2	< 2	< 3	< 2	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 2	< 2	< 2
110-189	Method Blank	< 2	< 3	< 2	< 4	< 3	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Average*		0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Standard Deviation		0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SRM 1941																	
110-072	SRM 1941	1400	450	52	40	100	740	240	1600	1500	570	730	1700	590	550	130	540
110-091	SRM 1941	1400	460	50	42	100	740	260	1700	1500	620	770	1800	620	590	140	560
110-111	SRM 1941	1500	470	63	49	130	910	320	2000	1700	660	840	1900	730	700	140	640
110-130	SRM 1941	1500	490	63	49	120	900	310	2100	1800	610	760	1700	670	620	140	580
110-155	SRM 1941	1400	470	54	43	110	810	270	1700	1500	600	770	1700	620	580	130	570
110-188	SRM 1941	1500	500	67	44	120	780	270	1700	1500	590	740	1700	670	660	150	630
Average*		1429.3	473.3	58.2	44.5	114.4	812.3	281.8	1800.0	1582.2	607.1	769.7	1761.3	651.4	616.7	137.5	586.0
Standard Deviation		57.8	18.4	6.4	3.3	9.4	68.2	28.7	168.5	141.7	26.3	37.4	80.9	46.1	50.9	7.1	39.1
SRM 1941 Certified concentrations (ng/g, dry wt)	$\bar{x}$	1322	406	115	52	104	577	202	1220	1080	550	---	1224	670	569	---	516
	95% CI	-------noncertified concentrations-------					59	42	240	200	79	---	239	130	40	---	83
	UCL						859	329	1971	1728	849	---	1975	1080	822	---	809
	LCL						337	104	637	572	306	---	640	351	344	---	281

NPH = naphthalene; 2MN = 2-methylnaphthalene; ACY = acenaphthylene; ACE = acenaphthene; FLU = fluorene; PHN = phenanthrene; ANT = anthracene; FLA = fluoranthene; PYR = pyrene; BAA = benz[a]anthracene; CHR = chrysene; BFLA = benzo[b]fluoranthene + benzo[k]fluoranthene; BAP = benzo[a]pyrene; IDP = indeno[1,2,3-cd]pyrene; DBA = dibenz[a,h]anthracene; BZP = benzo[ghi]perylene

$\bar{x}$ is the average concentration (ng/g, dry wt)
95% CI is the 95% confidence interval
UCL is the upper confidence limit (95% confidence limit + 35%)
LCL is the lower confidence limit (95% confidence limit - 35%)

*When an analyte was detected in some, but not all method blanks, the average concentration is based on the concentration when detected and one half the detection limit when not detected. When an analyte was not detected in any method blanks, zero is reported for the average.

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 1941

Organics in Marine Sediment

Standard Reference Material (SRM) 1941 is intended for use in validating analytical methods for the determination of trace levels of selected polycyclic aromatic hydrocarbons (PAHs) in marine sediments. Noncertified concentrations of additional PAHs, polychlorinated biphenyls (PCBs), and chlorinated pesticides are also provided. A unit of SRM 1941 contains approximately 70 g of sediment.

Certified Concentrations

Certified values for the concentrations of 11 PAHs naturally present in the sediment are provided in Table 1. These values are based on the results obtained from the analyses of this material using three different sample preparation procedures and analytical techniques based on gas chromatography with flame ionization detection, gas chromatography with mass spectrometric detection, and reversed-phase liquid chromatography with fluorescence detection. A summary of the analytical results obtained by using the different analytical techniques is provided in Appendix A. Noncertified concentrations for additional PAHs and for PCBs and pesticides are provided in Appendices B and C, respectively. Noncertified concentrations for trace element constituents are provided in Appendix D.

Table 1. Certified Concentrations of PAHs in SRM 1941

Compound	Concentration (μg/g dry weight)[a,b]
Phenanthrene	0.577 ± 0.059
Anthracene	0.202 ± .042
Pyrene	1.08 ± .20
Fluoranthene	1.22 ± .24
Benz[a]anthracene	0.550 ± .079
Benzo[b]fluoranthene	0.78 ± .19
Benzo[k]fluoranthene	0.444 ± .049
Benzo[a]pyrene	0.67 ± .13
Perylene	0.422 ± .033
Benzo[ghi]perylene	0.516 ± .083
Indeno[1,2,3-cd]pyrene	0.569 ± .040

[a] Concentrations are reported on a dry weight basis; material, as received, contains residual moisture.

[b] The certified values are weighted means of results from two or more analytical techniques. The weights for the weighted means were computed according to the iterative procedure of Paule and Mandel [1]. Each uncertainty is obtained from a 95% prediction interval plus an allowance for systematic error among the methods used. The allowance for systematic error is equal to the greatest difference between the weighted mean (certified value) and the component means for the analytical methods used. In the absence of systematic error, the resulting uncertainty limits will cover the concentration of approximately 95% of samples of this SRM having a minimum sample size of 5 g.

Gaithersburg, MD 20899
October 29, 1989

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

The second sentence of EPA Comment G1b states "All results were within the 95% confidence interval for the certified concentrations except for the following...." *The table then shows the UCL and LCL (with an incorrect column header which states 95% Conf. Int. instead of UCL-LCL range) and compares the NMFS to the UCL and LCL, not the 95% confidence interval that is certified by the NIST. Is this an intentional attempt to mislead potential users of the data as to the accuracy of the data?*

If NMFS compared their data to the appropriate 95% confidence interval instead of ±35% around that confidence interval, the table shown above in Comment G1b would have appeared as follows:

Sample Number	Analyte	Mean plus 95% Conf. Int. (ug/kg)	Trustee Result (ug/kg)	Trustee Data: Percent above Certified Mean plus 95% Conf. Int.
110-072	Phenanthrene	636	740	16.3
	Fluoranthene	1460	1600	9.6
	Pyrene	1280	1500	17.2
	Benzo(b)fluoranthene	1463	1700	16.2
110-091	Phenanthrene	636	740	16.4
	Anthracene	244	260	6.6
	Fluoranthene	1460	1700	16.4
	Pyrene	1280	1500	17.2
	Benzo(b)fluoranthene	1463	1800	23.0
110-111	Phenanthrene	636	910	43.1
	Anthracene	244	320	31.1
	Fluoranthene	1460	2000	37.0
	Pyrene	1280	1700	32.8
	Benzo(a)anthracene	629	660	4.9
	Benzo(b)fluoranthene	1463	1900	29.9
	Indeno(1,2,3-c,d)pyrene	609	700	14.9
	Benzo(g,h,i)perylene	599	640	6.8
110-130	Phenanthrene	636	900	41.5
	Anthracene	244	310	27.1
	Fluoranthene	1460	2100	43.8
	Pyrene	1280	1800	40.6
	Benzo(b)fluoranthene	1463	1700	16.2
	Indeno(1,2,3-c,d)pyrene	609	620	1.8
110-155	Phenanthrene	636	810	27.4
	Anthracene	244	270	10.7
	Fluoranthene	1460	1700	16.4
	Pyrene	1280	1500	17.2
	Benzo(b)fluoranthene	1463	1700	16.2
110-189	Phenanthrene	636	780	22.6
	Anthracene	244	270	10.7
	Fluoranthene	1460	1700	16.4

Sample Number	Analyte	Mean plus 95% Conf. Int. (ug/kg)	Trustee Result (ug/kg)	Trustee Data: Percent above Certified Mean plus 95% Conf. Int.
	Pyrene	1280	1500	17.2
	Benzo(b)fluoranthene	1463	1700	16.2
	Indeno(1,2,3-c,d)pyrene	609	660	8.4
	Benzo(g,h,i)perylene	599	630	5.2

As shown in this corrected table, when the NMFS data for SRM 1941 are compared against the certified 95% confidence interval, the are 35 occurrences of measurements falling above the upper 95% confidence interval, rather than the 5 occurrences reported in Comment G1b. There were no occurrences of measurements falling below the lower 95% confidence interval.

Instead of reporting their data according to commonly accepted procedures, the NMFS has made it easier for them to appear to be generating accurate data by adding an additional 35% to the 95% confidence intervals and assessing their data against this much larger range. It is not an accepted procedure under the CLP guidelines for data validation. NMFS results are recovery corrected results compared to surrogate recovery corrected limits established by NIST. NIST values are expected to be high compared to data generated using EPA methodology, since most EPA methods preclude recovery correction of reported analytical results. NMFS' results for NIST 1941 should be very comparable to NIST ranges since recovery correction has been done on both; however. NMFS performance shows high bias in comparison to the NIST certified ranges. This suggests that NMFS data are biased high in comparison to the universe of analytical laboratories.

Comment G1c: Surrogate Compound Recovery

The following surrogate compounds were added to each sample prior to extraction:

- d8-naphthalene
- d10-acenaphthene
- d12-benzo(a)pyrene

Surrogate compounds are compounds not expected to be present in samples but which exhibit chemical and chromatographic properties similar to analytes of interest. Surrogate compound recoveries monitor overall extraction and analytical efficiency and, thus, give an indication of analytical accuracy.

All surrogate compound recoveries for PAH analyses met project criteria of 50 - 125 % for all samples except one, number 110-153 with 128% recovery for d12-benzo(a)pyrene.

Based on surrogate compound recoveries, trustee data meet project accuracy requirements.